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A New Vogel-like Law: Ionic Conductivity, Dielectric Relaxation and Viscosity Near the Glass
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by

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A New Vogel-like Law: Ionic Conductivity, Dielectric Relaxation and Viscosity Near the Glass Transition

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ABSTRACT

A model, based on defect diffusion, is developed that describes temperature and pressure dependence of dielectric relaxation, ionic conductivity and viscosity of glass-forming liquids near the glass transition temperature. The resultant expressions for ionic conductivity are compared with experimental results for the polymer electrolytes poly(ethylene glycol) (PEG) and poly(propylene glycol) (PPG) containing LiCF_3SO_3 . Those for dielectric relaxation are compared with experimental results for poly(propylene oxide) (PPO) and poly(vinyl acetate). The theoretical viscosity law is compared to experiments on propylene carbonate (PC).

I. INTRODUCTION

In 1889, Arrhenius introduced the concept of an activation energy together with a law for the related characteristic relaxation time $\tau_A = \nu_0^{-1} \exp(\Delta/kT)$ where k is Boltzmann's constant and T is the absolute temperature. The Arrhenius law was later derived by Kramers in terms of the trajectory of a particle successfully crossing an energy barrier of height, Δ , with an attempt frequency of ν_0 . It is perhaps not as well known that this law is invalid for most glass-forming materials. A corresponding law for these materials,

$$\tau_v = A_v \exp\left(\frac{B_v}{T - T_0}\right), \quad (1)$$

was proposed by Vogel in 1921 and later by Fulcher, and Tammann and Hesse. Today this is often called the Vogel law or the VFT law or some other combination of the above. The interpretation of the parameters A_v , B_v and T_0 is not straightforward. First, one notices that T_0 is a special temperature where the time scale diverges. The temperature T_0 is typically well below T_g , the glass transition temperature of the material, *i.e.*, the relaxation dynamics are focused on T_0 and not on T_g . There have been several attempts to derive the Vogel law or alternative laws. Previously, we had derived, within a defect diffusion model, the following equation for zero (approximately atmospheric) pressure¹⁻³:

$$\tau_{DD} = A_{DD} \exp\left(\frac{B_{DD}}{(T - T_c)^{3/2}}\right) \quad (2)$$

where A_{DD} , B_{DD} and T_c are constants. The derivation of eq. (2) involves a somewhat novel route by initially arriving at a stretched exponential relaxation time distribution within a defect diffusion model. The time scale in the stretched exponential law depends on the mobile defect concentration. In this model, as the temperature is lowered, the number of mobile defects decreases and the material becomes more viscous (rigidity begins to set in). At T_g , rigidity percolates and the glassy state is formed. Relaxation, however, is still occurring. An “imminent” phase transition in the number of mobile defects, as the temperature is lowered towards T_c , creates the behavior characterized by eq. (2). The thermodynamic transition at T_c is never reached because ergodicity is lost at T_g .

Equation (2) is consistently as successful as (or more so than) the Vogel law (eq. 1) for fitting ionic conductivity, dielectric relaxation and viscosity data for glass-forming materials⁴⁻⁶ especially when the Vogel law fails to fit data adequately near T_g , and the system is sometimes said to show a “return” to Arrhenius behavior.²

The purpose of this Letter is to extend eq. (2) to include the effect of pressure. It will be demonstrated that the resultant generalized Vogel-type law, eq. (5) below, successfully describes

measurements of ionic conductivity in salt-containing, glass-forming liquids, such as those frequently used as the electrolyte in a battery. Finally, it is shown that the theory also accounts for dielectric relaxation and viscosity in several glass-forming materials.

II. THEORY

Consider an ion-containing glass-forming material possessing a concentration c of defects, where c_m of these are mobile. Assume an ion at a site is induced to hop at time t , due to the flux of defects, $F(t)$, into that site. To calculate $F(t)$ we employ a waiting time probability density, $\psi(t)$, for holding a defect for a time t , in between its jumps in order to incorporate a randomness into the defect motion. The defect flux into a site, within a time t , is $c_m N(t)$ where $N(t)$ is the number of distinct sites a single random walking defect visits within a time t . The ion-hopping probability distribution is¹⁻³ then identical to the relaxation law $\phi(t) = \exp(-c_m N(t))$. In this article, we shall generally retain the interpretation of $\phi(t)$ as a relaxation law, recognizing however, that the application of $\phi(t)$ to ion hopping problems is straightforward and direct. For a typical random walk, $N(t)$ is proportional to t and exponential relaxation or hopping occurs. The stretched exponential is another possibility, i.e.

$$\phi(t) = \exp(-\lambda c_m t^\beta) \equiv \exp(-[t/\tau_{DD}]^\beta) \quad (3)$$

with $\beta < 1$, λ constant and $\tau_{DD} = (\lambda c_m)^{-1/\beta} = c_m^{-1/\beta} \tau_o$. This is the typical behavior exhibited by glassy materials. There are several ways one can arrive at eq. (3). If the defect delays are related to overcoming a free energy barrier as follows: $t = t_0 \exp(+(\Delta - TS)/kT)$ then random distributions of energy barriers, Δ , and entropy barriers, S can generate a distribution of waiting times between jumps, with an infinite mean, i.e. $\psi(t) \approx 1/t^{1-\beta}$ with $\beta < 1$, leading to $N(t) \approx t^\beta$. Since only the defects are mobile in the model, as the temperature is lowered, the defects may cluster (or correlate their motion) to lower the system entropy. We now assume that single isolated defects, of concentration c_1 , are more mobile than any cluster of defects. We therefore

replace c_m in eq. (3) by c_1 . To have a single defect at a site, one must first have a defect there with probability c and also have all of the z “neighbor” sites within its correlation volume unoccupied, i.e. $c_1 = c(1-c)^z$, with $z = (\xi/d)^3$, where ξ is the defect-defect pair correlation length, and d is the nearest-neighbor lattice spacing. In a mean field lattice gas model, the correlation length ξ between the defects grows near and above the critical temperature T_c as

$$\xi(T) \approx L \left(\frac{T_c}{T - T_c} \right)^{1/2} \text{ where } L \text{ is a constant and } T_c \text{ is the temperature at which single defects}$$

disappear and below which only defect clusters exist. With increasing pressure, the nearest-neighbor spacing, d , is assumed to decrease as $d^3 = d_0^3(1 - \delta(T, P))$ where $1 - \delta(T, P) = V(T, P)/V(T, 0)$ is the fractional volume change of the material as pressure increases and d_0 is the mean lattice spacing separation at zero pressure. The time scale in the stretched exponential can now be expressed as,

$$\tau_{DD} \approx c_1^{-1/\beta} \tau_0 = c^{-1/\beta} \tau_0 \exp \left(\frac{BT_c^{3/2}}{(T - T_c)^{3/2} (1 - \delta(T, P))} \right) \quad (4)$$

where $B = -(L/d_0)^3 \ln(1-c)/\beta$. This represents a new relaxation (or hopping) law that is Vogel-like, but with a 3/2 temperature exponent and the inclusion of pressure effects. Note that T_c is in general a function of P . In the above model, the critical temperature T_c plays a role analogous to the Kauzmann temperature, T_k . It is the thermodynamic transition temperature at which the extra entropy of the melt is lost, and like the Kauzmann transition, the demixing transition at T_c never occurs in a real system because T_g intervenes (i.e., rigidity percolates) first. Evidence for a demixing transition is clearly seen in the spatial heterogeneity found in all fragile glasses near T_g .¹⁹

Since the time scales for ion hopping and relaxation are both given by eqn. 4 above, a model of conductivity can be developed as follows. Although an individual defect may have an infinite waiting time between jumps, ion hopping, induced by the defect flux follows a stretched

exponential waiting time distribution law, whose first moment, τ_1 is finite. Since the ion diffusion constant is of the form $D = \frac{l^2}{6\tau_1}$, employing the Nernst-Einstein relation $\sigma = \frac{q^2 n D}{kT}$, where q is the charge on an ion and n is the ion concentration, we can, using eqn (4), derive an expression for the conductivity $\sigma(T, P)$

$$\sigma(T, P) = \frac{q^2 n l^2 c^{1/\beta}}{6kT\tau_0} \exp\left(\frac{-BT_c^{3/2}}{(T-T_c)^{3/2}(1-\delta)}\right) \quad (5)$$

Basically, as the pressure is increased, defects are pushed closer together and become more clustered leaving fewer single (mobile) defects. This will decrease the defect flux, increasing the time scale τ_i , and thus decreasing the conductivity σ . Single defect transport, of course, is anomalous and a diffusion constant for the defect motions cannot be defined in the normal way, while the subordinated ion motion is well-defined.

An approximate equation for the viscosity, η , follows by applying the Stokes-Einstein equation $\eta = \frac{kT}{6\pi D r_0}$, where r_0 is the effective molecular radius. We recognize that the Stokes-Einstein relation breaks down for fragile glasses near T_g , and it is used here merely to derive an approximate viscosity relation.²⁰

III. COMPARISON WITH EXPERIMENT

A. Dielectric Relaxation

For the purpose of comparing the theory of dielectric relaxation with experiment, eq. (4) is employed. The pre-exponential is defined to be $c^{-1/\beta}\tau_0 \equiv A_\tau$. For the present analysis, both A_τ and B are taken to be constant. In addition, it is assumed that the volume of the material changes with pressure according to:

$$1-\delta = 1 - \chi(T)P + f(T)P^2 + g(T)P^3. \quad (6)$$

This form is chosen as it is supported by the PVT data of Zoller and Walsh.⁷ Finally, the critical temperature is assumed to be pressure dependent according to:

$$T_c(P) = T_c + \left(\frac{\partial T_c}{\partial P}\right)P + \frac{1}{2}\left(\frac{\partial^2 T_c}{\partial P^2}\right)P^2 \quad (7)$$

where T_c with no pressure argument refers to the critical temperature at zero pressure. This functional form is chosen since, as will be shown, there appears to be a relationship between T_c and T_g and it is well known that there is usually a significant amount of curvature in the shift of T_g with pressure. Equations 6 and 7 are employed here simply as empirical relationships, which have been used by other investigators. PVT data for glass-forming materials is often directly fitted to eq. 6, which is thus also conveniently available for fitting the model eq. 4. The analog of eq. 7 for T_g has also been used by experimenters to fit data and, in light of the scaling found between T_c and T_g , it also seems a natural first choice for modeling the pressure dependence of T_c . The spirit of our approach is a Landau-type treatment of local free energy fluctuations, which can be expected to provide a useful approximation until one gets very close to T_c . Since T_c is never reached in glass-formers (due to T_g intervening), analytic Landau expansions should work reasonably well in the experimentally-accessible P-T range away from T_c .

1. Zero Pressure Temperature Variation

Equation (4) was best-fit to previously reported dielectric relaxation data at 1 atm for PPO⁸ and poly(vinyl acetate) (PVAc)⁹ and new data for poly(propylene glycol) of average molecular weight 1025 (PPG). The best-fit parameters are listed in Table I along with the rms deviations for both eq. (4) and the VFT equation (eq. (1)). The goodness of fit for the 1 atm dielectric relaxation data is about the same for eq. (4) and the VFT equation. A fragility plot of the data and best-fit curve for PPG is shown in Fig. 1. The agreement between theory and experiment is quite good.

2. Zero Pressure Slope

Experimental values for the pressure derivative of the dielectric relaxation time (or reciprocal of the peak frequency, $\tau = 1/\omega_{\max} = 1/2\pi f_{\max}$) at P=1.0 atm in PPO and PVAc have been reported.^{13,15} The prediction of eq. (4) for this quantity is

$$\left(\frac{\partial \ln f_{\max}}{\partial P}\right)_T = \frac{\chi B T_c^{1.5}}{(T - T_c)^{1.5}} - \frac{1.5 B T T_c^{0.5}}{(T - T_c)^{2.5}} \left(\frac{\partial T_c}{\partial P}\right) \quad (8)$$

This equation was best-fit to the data allowing $(\partial T_c / \partial P)$ to vary. The experimental results and best-fit curves are shown in Fig. 2. The agreement between the theory and experiment is quite good.

The best-fit values of $(\partial T_c / \partial P)$, 104K/GPa for PPO and 204K/GPa for PVAc, are interesting because $(\partial T_g / \partial P)$ has been measured for these materials. Those values are 196K/GPa and 266K/GPa for PPO¹⁰ and PVAc,^{15,16} respectively. In both cases, $(\partial T_c / \partial P)$ is less than $(\partial T_g / \partial P)$. That is not surprising since T_c , itself, is less than T_g . Furthermore, $(\partial T_c / \partial P)$ scales with $(\partial T_g / \partial P)$.

3. Zero Pressure Curvature

Next, the experimental values of $(\partial^2 \ln f_{\max} / \partial P^2)_T$ for PPG vary from about -17 to -53 GPa⁻² as the temperature decreases from 273 to 237K.⁸ PVAc, on the other hand, shows no curvature.¹⁰ The present theory accounts for these results and differences since an equation for $(\partial^2 \ln f_{\max} / \partial P^2)$ can be easily calculated from eq. (4).

It is of interest to compare the pressure curvatures in T_c and T_g . The experimental values for $(\partial^2 T_g / \partial P^2)$ are -340 and -1340 K/GPa² for PPO^{11,12} and PVAc,^{10,13} respectively. Consequently, the values of $(\partial^2 T_c / \partial P^2)$ are both smaller than and scale with $(\partial^2 T_g / \partial P^2)$. This also suggests a relationship between T_c and T_g . The implications of these results will be discussed further in section IV.

B. Ionic Conductivity

For the purpose of comparing the theory of the ionic conductivity with experiment, eq. (5) was used defining $A_\sigma \equiv (q^2 n l^2 c^{1/\beta}) / 6 k \tau_o$ and assuming that it is constant. Also, $(1-\delta)$ was included in the denominator of the pre-exponential to account for an increase in ion concentration as pressure increases.

1. Temperature Variation of Conductivity at Zero Pressure

Equation (5) was best fit to the zero pressure ionic conductivity data for several electrolytes^{5,6,14} using a non-linear least squares approximation. The best-fit parameters are listed in Table I and the data and best-fit curve for PPG:LiCF₃SO₃ are shown in Fig. 1. The fit to the data is quite good.

2. Pressure Variation of the Ionic Conductivity

Following a procedure similar to that described in Part A, the theoretical equation for $(\partial \ln \sigma / \partial P)$ was best-fit to the experimental data for PPG:LiCF₃SO₃⁶ and PEG:LiCF₃SO₃⁸ allowing $(\partial T_c / \partial P)$ to vary. The best-fit values of $(\partial T_c / \partial P)$ are 94 and 64 K/GPa for the PPG- and PEG-based materials, respectively.

Next, it was found that values of $(\partial^2 T_c / \partial P^2) = -179$ and -134 K/GPa² for PPG:LiCF₃SO₃ and PEG:LiCF₃SO₃, respectively, reproduce the experimental data for $(\partial^2 \ln \sigma / \partial P^2)$.

Finally, using these input parameters, the theoretical values for $\ln \sigma$ vs. pressure at three temperatures were calculated using eq. (5) and the results are shown with the experimental results in Fig. 3. The agreement between theory and experiment is quite good.

C. Viscosity

The zero pressure data for propylene carbonate (PC) reported elsewhere⁵ were best fit to the viscosity equation (see the discussion following eq. (5)). The results are presented in Table I. The factor of T in the pre-exponential results in a small reduction in the rms deviation over eq. (2) and consequently is even better than the fit using the VFT equation.⁵ We note that the

agreement between the fitted T_c and the experimental T_k is excellent.²¹ In fact the T_c found is much closer to T_k than is T_0 . This supports our view (see below) that the transitions represented by T_c and T_k are the same or closely related. Uncertainties in the experimental values of T_c , T_0 , and T_k are well-documented²¹ and further systematic experiment and analysis of well-characterized materials are needed.

IV. DISCUSSION

As with the Vogel law, a feature of the present model is the existence of an underlying critical temperature, T_c . There have been a number of detailed discussions concerning the relationship between T_0 and T_k , the Kauzmann temperature.¹⁵⁻¹⁷ In fact, one of the main justifications for eq. (1) is that T_0 and T_k are about the same. For convenience, the values of T_0 for the present materials are also listed in Table I. It is clear that for all but PEG:LiCF₃SO₃ T_c is relatively close to (12-20K below) T_0 . Since it has been concluded that T_0 is close to T_k ,¹⁵⁻¹⁷ it follows that T_c should also be close to T_k . PC is the only material in the present work studied by the authors for which the Kauzmann temperature is known.^{17,21} The value quoted there is 125.8 K which compares very well with the value of $T_c = 123.7$ K. Consequently, it will be of considerable interest to apply the formalism developed in the present work to other materials for which T_k is known. T_c is in fact closer to T_k than is T_0 for this material.²¹

In the present application of the model, five adjustable parameters were used, namely B , a prefactor, and T_c and its first two pressure derivatives. However, the results of the analysis suggest that a good representation of the dielectric relaxation data can be achieved by as few as one adjustable parameter, B . The reasons are as follows. First, it is clear that the pre-exponential is approximately constant at -11.3 . This may be a universal constant, at least for relaxations in the vicinity of room temperature. Next, the value of T_c can be estimated from the experimental value of T_g . The reason for this is that the data show that $(T_g - T_c)/T_g \approx 0.25$. Further, the values of $(\partial T_c / \partial P)$ and $(\partial^2 T_c / \partial P^2)$ appear to scale with T_g . Consequently, to a first approximation, all necessary parameter values associated with T_c can be inferred from PVT data.

The consequence, of course, is that the only remaining adjustable parameter is B . Interestingly, the experimental values of B are approximately the same for the structurally related materials (propylene glycols and propylene carbonates). The value of B is different for PVAc. This suggests that B reflects the structure of the material and this would be consistent with the theory since B comprises terms such as the defect-defect correlation length, the defect density, and the defect barrier.

At present we recognize that the above theory of ionic conductivity remains phenomenological. However, it represents significant progress, since previous treatments utilized the concept of an activation volume that, as has been pointed out several times,^{6,18} is not applicable to materials exhibiting Vogel-type behavior.

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Table I. Parameters relevant to the defect diffusion model.

	Ionic Conductivity		Dielectric relaxation			Viscosity
	PPG: LiCF ₃ SO ₃	PEG: LiCF ₃ SO ₃	PPG (1025)	PPO (Parel)	PVAc	PC
Log ₁₀ (A_i)	0.973	1.31	-11.3	-11.2	-11.3	6.35
(A_σ and A_τ have units of S-K/cm and s, respectively.)						
B	7.84	5.28	4.45	4.18	6.08	4.71
$T_c(K)$	150.1	148.0	156.3	160.1	227.9	123.7
$T_g(K)$	218	203	206	211	304	166
$T_o(K)$	172.3	181.7	168.2	172.7	249.2	136.9
Temp Range of The Data (K)	218-345	264-328	206-229	216-232	318-358	157-343
rms dev	0.012	0.002	0.006	0.004	0.015	0.113
rms dev (VFT)	0.033	0.002	0.006	0.004	0.015	0.189

FIGURE CAPTIONS

Figure 1. Electrical resistivity for PPG:LiCF₃SO₃ and electrical relaxation time for PPG 1025 vs. reciprocal temperature.

Figure 2. Pressure derivative of the frequency of the maximum in the electrical relaxation peak (reciprocal of the relaxation time) at P=0 for PPO (Parel Elastomer) and PVAc vs. temperature. The points are experimental and the lines are theoretical.

Figure 3. Electrical conductivity vs. pressure for and PPG:LiCF₃SO₃ at various temperatures. The points are experimental. The squares represent decreasing pressure and the circles are increasing pressure. The lines are predicted by the generalized Vogel equation.

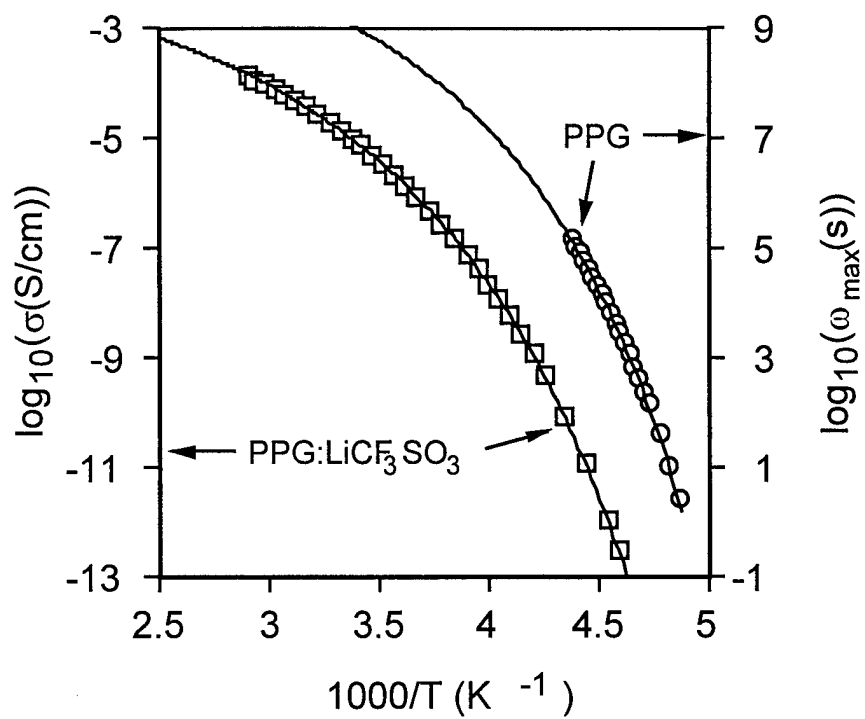


Figure 1

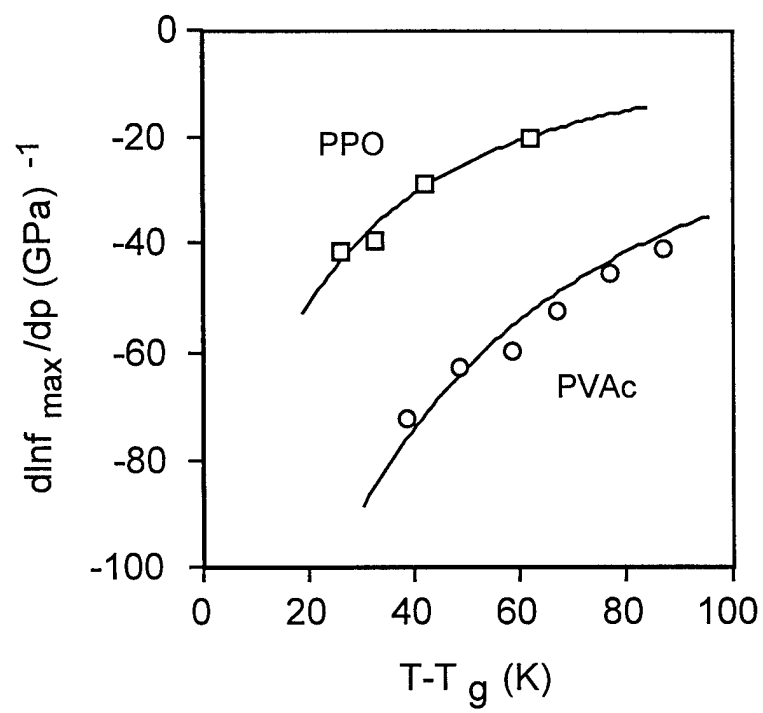


Figure 2

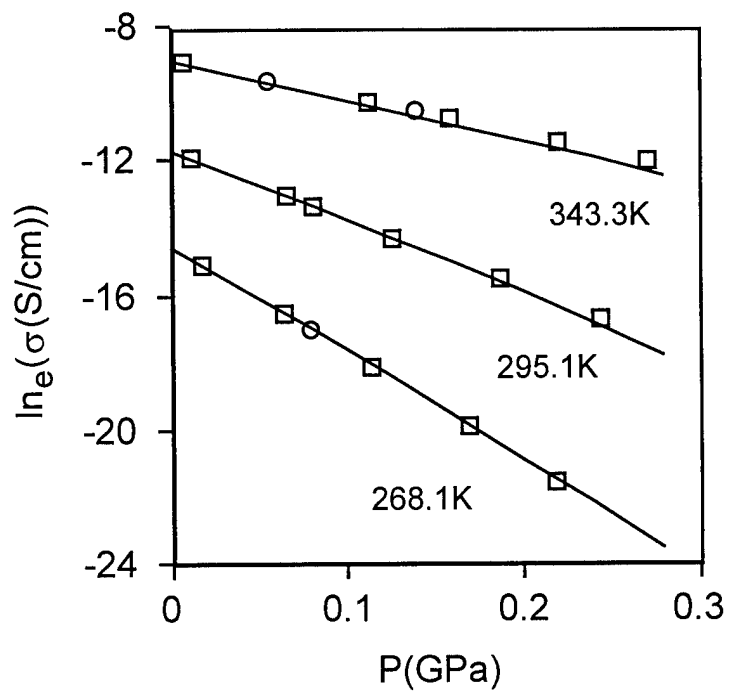


Figure 3